Received: 20 July 2009 Revised: 11 December 2009 Accepted: 17 December 2009 Published online in Wiley Interscience: 9 March 2010

(www.interscience.wiley.com) DOI 10.1002/jsfa.3915

Utilisation of corn (*Zea mays*) bran and corn fiber in the production of food components†

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Abstract

The milling of corn for the production of food constituents results in a number of low-value co-products. Two of the major co-products produced by this operation are corn bran and corn fiber, which currently have low commercial value. This review focuses on current and prospective research surrounding the utilization of corn fiber and corn bran in the production of potentially higher-value food components. Corn bran and corn fiber contain potentially useful components that may be harvested through physical, chemical or enzymatic means for the production of food ingredients or additives, including corn fiber oil, corn fiber gum, cellulosic fiber gels, xylo-oligosaccharides and ferulic acid. Components of corn bran and corn fiber may also be converted to food chemicals such as vanillin and xylitol. Commercialization of processes for the isolation or production of food products from corn bran or corn fiber has been met with numerous technical challenges, therefore further research that improves the production of these components from corn bran or corn fiber is needed.
Published 2010 by John Wiley & Sons, Ltd.

Keywords: maize; co-products; corn fiber gum; vanillin; ferulic acid; xylo-oligosaccharides

INTRODUCTION

Corn (*Zea mays*) is a major crop in the USA, with 329×10^6 t produced domestically in 2008.[1] In comparison, 68.0×10^6 t of wheat and 9.24×10^6 t of rice were produced in 2008.[2,3] Of the total domestic corn use, 52% was devoted to animal feed, 37% went to ethanol production (fuel and beverage) and 11% was allocated for the production of food products.[4]

The processing of corn for food use requires one of two milling techniques: dry-milling or wet-milling. Corn dry-milling involves the traditional milling of clean, tempered grain (moisture content 200 g kg^{-1}) to separate its component parts: endosperm, germ and bran.[5,6] The major purpose of dry-milling is to recover the endosperm fraction for use as corn grits, meals and flours, while the germ may be harvested for oil.[6] Corn bran, however, currently has low value and is often used for animal feed alone or in combination with corn germ cake or meal (germ after oil has been pressed or extracted). Wet-milling of corn involves first steeping the grain in water and sulfur dioxide. During this process the moisture content increases to about 450 g kg^{-1} and the kernels are softened to facilitate separation of the components: starch, gluten, fiber and germ.[7] The profitable products of wet-milling are the starch (endosperm) and oil (germ) from the corn kernel. Co-products of wet-milling include corn fiber, corn gluten and steeping solids, which are sometimes combined and sold as corn gluten feed.[7] Both corn bran and corn fiber are mainly composed of the pericarp (bran); however, corn fiber also contains cell wall material from the endosperm, which is not contained in corn bran.[8]

Corn bran is produced in yields of about 60–70 g kg^{-1}, while corn fiber is produced in yields of about 80–110 g kg^{-1} total corn kernel.[9,10] In 2008, 25.6×10^6 t of corn was wet-milled, while 5.24×10^6 t was dry-milled.[4] Thus about 2.43×10^6 t of corn fiber and 0.341×10^6 t of corn bran were produced.

Traditional uses for these co-products of corn processing largely include animal feed, which does not command a high price. Therefore research is constantly under way to expand the use of these products. Lucrative applications of these products would provide much needed economic relief for farmers by increasing revenue and would benefit manufacturers and consumers by decreasing fuel and food costs. Much of the research concerning the utilization of corn bran and corn fiber has centered on its conversion to fuel ethanol;[11,12] however, food applications of these co-products may also provide added value. Therefore in this review the composition of corn bran and corn fiber will be discussed and then current and prospective research surrounding the utilization of corn fiber and corn bran in the production of food components will be addressed.

COMPOSITION OF CORN BRAN AND CORN FIBER

The chemical composition of corn bran and corn fiber is shown in Table 1. Clearly, the majority of both corn bran and corn fiber is dietary fiber, which is nearly completely insoluble. The insoluble dietary fiber in corn bran is composed of cellulose (~280 g kg^{-1}) and hemicellulose (~700 g kg^{-1}), with only a small amount of

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† *Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture.*

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Table 1. Composition (g kg^{-1}) of corn bran and corn fiber

Constituent	Corn bran	Corn fiber
Protein[a]	50–115[13–15]	100–130[16,17]
Starch	40–112[13,14]	150–200[16,17]
Oil	13.2–19[14,18]	17.2–36.8[18]
Ferulate phytosterol esters[b]	0.2[18]	0.61–1.28[18]
Ash	6–10[14,15]	6–20[16,17]
Total dietary fiber	732–860[13,19,20]	526–735[21]
Soluble fiber	2–26[19,20]	ND–3[21]
Insoluble fiber	706–863[19,20]	526–732[21]
Arabinose[c]	128–178[13,14]	113–117[12,16]
Xylose	217–243[13,14]	176–213[12,16]
Mannose	3[15]	ND–8.4[21]
Galactose	44–51[13–15]	35.9[16]
Glucose[d]	182–248[13,15]	300–372[12,16]
Uronic acids	39–42[13–15]	30–40[17]
Lignin	7–10[13,14]	78[16]
Total phenolics	55[13]	NR
Ferulic acid	28–31[13–15]	1.02–18.5[22,23]
Diferulic acid	6.8–32[15,24]	NR
p-Coumaric acid	3–4[13,14]	2[22]

ND, not detected; NR, not reported.
[a] Nitrogen × 6.25.
[b] Indentation indicates that this component is a component of the above constituent but is still reported as a proportion of the entire corn bran or corn fiber product.
[c] Neutral sugars and uronic acids reported in polysaccharide form.
[d] non-starch glucose.

lignin (~10 g kg^{-1}). The hemicellulosic fraction is composed of a β-(1 → 4)-xylopyranosyl backbone and α-L-arabinofuranosyl residues as side units linked (1 → 2) or (1 → 3) to the main chain.[14] Side units of D-glucuronic acid or oligosaccharide side chains containing galactose, xylose and arabinose also occur.[25,26] Some of the arabinofuranosyl side units contain a ferulic acid moiety esterified to O-5.[13,27,28] Because of its complex structure, this hemicellulosic fraction may be referred to as a heteroxylan or, because the structure is mainly composed of xylosyl and arabinosyl units, an arabinoxylan. Saulnier and Thibault[29] elegantly described the interactions between these heteroxylans and other cell wall components within corn pericarp: the heteroxylan fraction fills the spaces between the cellulosic microfibrils, which are then crosslinked with each other and other cell wall components via di- and triferulate bridges, solidifying the cell wall's structure and rendering the heteroxylan insoluble.

The remainder of corn bran and corn fiber comprises residual starch, lipid, protein, ash, phenolic compounds and other trace phytochemicals (Table 1). Subtle differences in the amounts of these components are apparent. Most notably, corn fiber contains more than twice as much ferulate phytosterol esters, which can be recovered in corn fiber oil,[18] while corn bran contains two times more ferulic acid.[23] The importance of these compounds will be discussed further in later sections.

UTILISATION OF WHOLE CORN BRAN AND CORN FIBER

Research on the utilization of corn-milling co-products in food products began with the addition of corn bran to breads,[30] cakes[31] and muffins[32] with the aim of increasing the dietary fiber content of widely consumed foods. Unfortunately, this resulted in undesirable changes in product quality: bread containing corn bran at 200 g kg^{-1} flour showed a 20% reduction in loaf volume,[30] layer cakes containing corn bran at 300 g kg^{-1} flour showed decreases in most sensory scores, including texture, color and flavor,[31] and corn bran at 250 g kg^{-1} flour in muffins resulted in significant decreases in flavor, mouthfeel, texture and overall acceptability compared with muffins containing the same level of wheat bran.[32]

In more recent experiments, Mendonca *et al*.[33] found that corn bran significantly decreased the radial expansion ratio, appearance and general acceptability of extruded snacks containing corn bran at 150–320 g kg^{-1}. Holguin-Acuna *et al*.[34] substituted corn bran for oat flour in an extruded breakfast cereal. They found that corn bran at 300 and 400 g kg^{-1} gave the lowest breaking strength, and tested these two cereals in a sensory panel. Panelists preferred the cereal that contained corn bran at 300 g kg^{-1}. Unfortunately, the authors did not compare this sample with a control product containing no corn bran.

Artz *et al*.[35] hypothesized that the poor performance of corn bran in baked goods could be improved by extrusion.[36] Therefore they extruded corn bran using a twin-screw extruder[37] and then incorporated the extruded corn bran into cookies. Unfortunately, panelists were able to correctly identify the odd sample in triangle tests comparing control cookies with cookies containing extruded corn bran but were not able to correctly identify the odd sample in triangle tests comparing cookies containing extruded or unextruded corn bran,[35] indicating that extrusion did not change the baking properties of corn bran in this application.

In attempts to utilize other cereal brans, treatments such as careful control of particle size[38,39] and enzyme treatment[40] have shown some promise; therefore these treatments with corn bran or corn fiber may also be beneficial, although perhaps not directly applicable.

De Kock *et al*.[38] and Ozturk *et al*.[39] demonstrated that bran particle size affects quality when added to bread and cookies. In bread, smaller particle sizes decreased loaf volume more than larger particle sizes.[38] In cookies, medium (212–425 μm) and coarse (425–850 μm) particle sizes gave better spread ratios, color and overall sensory scores compared with cookies made with finer particle sizes (<212 μm).[39]

Enzyme treatment may also affect the quality of baked goods with added cereal brans. The best example of this is the use of *endo*-(1 → 4)-β-xylanases (xylanases; EC 3.2.1.8) in bread making. During bread making, the presence of insoluble arabinoxylans increases water absorption[41–43] and decreases loaf volume,[44] thus diminishing bread quality. Soluble arabinoxylans have a positive impact on bread quality owing to their contribution to dough viscosity, air entrapment and the improvement of loaf volume and texture.[41,45–47] Xylanase addition to bread dough can convert a portion of the insoluble arabinoxylans to soluble oligosaccharides and improve loaf volume.[48,49] Because corn bran and corn fiber contain substantial levels of arabinoxylans (Table 1), adding xylanase to bread fortified with corn bran or corn fiber may improve its loaf volume and sensory attributes. This may also extend to other products such as cookies.[40]

ISOLATION AND UTILISATION OF COMPONENTS OF CORN BRAN AND CORN FIBER

Corn bran and corn fiber contain potentially valuable components, including oil, phytosterol esters, dietary fiber and phenolic

antioxidants. Therefore some researchers have explored the use of processing technologies to harvest these components. Research on the extraction, production and utilization of each of these components will be discussed separately.

Cellulosic fiber gel

Corn bran contains about 200 g cellulose kg^{-1} (Table 1). Usually, cellulose exhibits undesirable characteristics in foods and has few desirable functional properties;[50] however, the native structure may be disrupted in a two-stage high-shear process to yield a cellulosic fiber gel.[51,52] The first stage involves treatment with a base to completely disintegrate the cell wall structure of corn bran. The solids are then recovered and treated again with hydrogen peroxide to produce a colorless product. Cellulosic fiber gel from corn bran exhibits high hydration capacity, high viscosity and a gel-like structure.[53]

Cellulosic fiber gel from corn bran has found commercial success. Marketed under the trade name Z-Trim, it is promoted as a fat mimetic or flour substitute and is used in baked goods, condiments, dairy foods and processed meats (http://www.ztrim.com). Furthermore, Z-Trim is finding applications in school lunches to help meet the strict nutritional guidelines outlined in the National School Lunch Program set forth by the Food and Nutrition Service of the US Department of Agriculture.[54]

One example of Z-Trim's success was reported by Warner and Inglett.[55] Brownies prepared with Z-Trim containing 40% less fat than control brownies and 50% flour replacement were evaluated by trained panelists. The Z-Trim brownies were rated as not significantly different from the control brownies with respect to chocolate flavor, sweetness, bitter flavor, staleness and cereal flavor. In addition, the Z-Trim brownies rated significantly higher for moistness, density and cohesiveness, which are desirable characteristics in a fudge-like brownie.

Corn fiber gum

As mentioned, the dietary fiber fraction in both corn bran and corn fiber is composed largely of heteroxylan, which is insoluble owing to its di- and triferulate crosslinks.[28] A substantial portion of this heteroxylan may be removed by treatment of corn fiber or corn bran with alkali or alkaline hydrogen peroxide followed by acidification to pH 4.0–4.5 (to remove insoluble hemicellulose A) and ethanol precipitation.[10,14] The product thus obtained has been termed corn fiber gum.[26]

A myriad of treatment conditions have been used to solubilize corn fiber gum. Chanliaud *et al.*[14] used response surface experimental design in two experiments studying the effects of alkali type and concentration, time, temperature and liquid/solid ratio on corn fiber gum yields. When using potassium hydroxide, maximum yields of about 870 g kg^{-1} of available heteroxylan were obtained with alkali concentrations between 1.2 and 1.5 mol L^{-1} at 100 °C. Using saturated calcium hydroxide, maximum yields similar to those with potassium hydroxide were obtained after 19 h at 97 °C.

Hespell[17] found that potassium hydroxide and ammonium hydroxide produced dark extracts, probably due to colored compounds produced at the high temperatures used for extraction. This phenomenon was also shown with sodium hydroxide.[56] These dark-colored heteroxylan products would likely be undesirable owing to their influence on product color.[10] Calcium hydroxide produced a corn fiber gum that was free of impurities, lighter in color and dissolved easily in water.[17] Unfortunately, yields were low (<380 g kg^{-1} of available heteroxylan) and the cellulose-rich residue remaining after corn fiber gum extraction was hard and unusable. Higher yields with greater purity were obtained when corn fiber gum was extracted with potassium hydroxide and then the extract was treated with calcium hydroxide.

Another approach to producing a lighter-colored corn fiber gum has been to use hydrogen peroxide. This converts much of the colored lignin compounds to soluble organic acids that can be removed.[57] Delignification occurs optimally at pH 11.5;[57] therefore hydrogen peroxide can be added to the alkali during extraction[10] or the solubilized corn fiber gum may be treated with hydrogen peroxide after extraction,[58] the latter being more efficient.

As stated previously, corn fiber includes cellular material from the whole grain, while corn bran is composed mainly of the pericarp and does not include the cell wall material from the endosperm. Thus differences in structure or physical properties may occur between corn fiber gums isolated from these two milling co-products, depending on whether heteroxylans from the endosperm have different characteristics than those in the pericarp. Yadav *et al.*[59,60] isolated corn fiber gum from corn bran and corn fiber using the same extraction procedure, allowing for direct comparison. They boiled each starting material in dilute sodium hydroxide and calcium hydroxide. The soluble extract was then treated with hydrogen peroxide and partially acidified and the corn fiber gum was recovered by ethanol precipitation. They termed this isolate CFG-1. The residue left after dilute alkali extraction was further extracted with a more severe alkaline hydrogen peroxide treatment to obtain CFG-2.

Few differences in chemical composition and physical properties between these four fractions (CFG-1 and CFG-2 from corn bran and corn fiber) were evident.[59,60] The molecular weights of the two CFG-1s were 290 000 and 334 000 Da when isolated from corn bran and corn fiber respectively, while the molecular weights of the two CFG-2s were 491 000 and 452 000 Da respectively. Corn fiber gums isolated from both sources showed low viscosities, with CFG-1 and CFG-2 from corn bran being slightly lower than CFG-1 and CFG-2 from corn fiber. The arabinose/xylose ratios of CFG-1 and CFG-2 isolated from corn bran were 0.55 and 0.60 and from corn fiber 0.70 and 0.67 respectively. This suggests that heteroxylans originating from the endosperm are slightly more branched than those from the pericarp owing to the higher arabinose/xylose ratios in heteroxylans from corn fiber (which contained endosperm heteroxylans) compared with corn bran (which did not contain endosperm heteroxylans). This was further substantiated when the heteroxylan fraction was isolated from coarse corn fiber (corn fiber without the endosperm fraction), which gave arabinose/xylose ratios of 0.60 and 0.64 for CFG-1 and CFG-2 respectively.[59] Therefore subtle differences in heteroxylan branching may exist between endosperm and pericarp heteroxylans, although these minor differences are certainly not as varied as for heteroxylans from other grains such as wheat.[61]

Perhaps the most substantial difference between the corn fiber gums isolated from these two co-products was that both CFG-1 and CFG-2 from corn fiber were significantly better emulsifiers than the same products isolated from corn bran. In fact, Yadav *et al.*[59] showed that these CFGs were better emulsifiers than gum arabic in orange oil emulsions. They attributed this to the higher protein content of the samples originating from corn fiber. This suggests that proteins may be more intimately associated with heteroxylans in the endosperm than in the pericarp.

Recently, Carvajal-Millan *et al.*[24] and Yadav *et al.*[62] showed that some ferulic acid remains esterified to solubilized corn fiber gum

after alkali treatment. This is an important finding for two reasons. First, in the presence of hydrogen peroxide and peroxidase, corn fiber gum that contains ferulic acid can form gels via oxidative crosslinking, which can substantially affect its physical properties and potential applications.[63] Second, ferulic acid has received considerable attention owing to its antioxidant properties, and ferulic acid bound to soluble corn bran gum may be particularly important for delivering beneficial antioxidants to the colon for disease prevention. Indeed, while free phenolics are rapidly absorbed in the upper gastrointestinal tract,[64] bound phenolics can be released by microbial esterases in the lower gastrointestinal tract[65] and provide radical-scavenging activity in this region of the colon,[66] a region chronically under oxidative attack[67,68] and prone to disease.[69]

Corn fiber gum has not enjoyed the commercial success that has been afforded cellulosic fiber gel (discussed above). Because this product has several promising characteristics similar to those of exudate gums,[70] such as emulsification[60] and gel formation,[63] as described above, more research aimed at broadening the applications of this polysaccharide gum may eventually lead to commercialization as the market base widens. New applications could explore its use in expanded snacks, baked goods, beverages, specialty foods, edible coatings, supplements and the like.

Xylo-oligosaccharides

Xylo-oligosaccharides (XOS) are partially hydrolyzed, water-soluble xylan fragments that may be obtained from corn bran, corn fiber and other agricultural products by enzymatic or high-temperature treatment.[71,72] Enzymatic treatment proceeds by utilizing microbial xylanases, while high-temperature processing employs hydronium ions and organic acids generated *in situ* at high processing temperatures (160–220 °C) to partially hydrolyze heteroxylan polymers and yield soluble hydrolysates.[71,72]

Few studies exist on the use of corn bran or corn fiber as starting material for the enzymatic production of XOS. Research on the production of XOS from other cereal brans has revealed that 250–450 g kg^{-1} of available heteroxylan may be released from the starting material with xylanase treatments, depending on processing conditions.[73,74] However, previous researchers have shown that corn bran or corn fiber heteroxylan is a more difficult substrate for enzymatic degradation compared with others such as wheat bran.[23] Therefore new xylanases that are more specific for corn heteroxylan are needed.

One of the most important factors to consider in the enzymatic production of XOS from agricultural products is substrate selectivity of the xylanase. Direct enzymatic hydrolysis requires xylanases with high substrate selectivity toward insoluble xylan. Moers *et al*.[75] screened xylanases from *Bacillus subtilis, Aspergillus aculeatus, Aspergillus niger, Trichoderma viride* and *Trichoderma longibrachiatum* for their activities on soluble and insoluble xylan substrates. They found that the enzyme preparations from *B. subtilis* and *A. niger* were the most active on insoluble substrates, while those from *A. aculeatus* and *T. virde* were the most active on soluble xylan. Xylanases are also classified into a number of families based on their catalytic activity.[76] Xylanases from families 10 and 11 are active on heteroxylans such as those in corn bran.[76] For the production of XOS, family 11 may be more desirable owing to lower production of xylose,[77] although family 10 is more able to hydrolyze highly branched arabinoxylans.[78]

Some researchers have shown that the enzymatic production of XOS can be increased by adding accessory enzymes. For instance, de Vries *et al*.[79] showed that arabinofuranosidases (EC 3.2.1.55) from *Aspergillus* fungi resulted in a 2.0–2.5-fold increase in the release of xylan. A feruloyl esterase (EC 3.1.1.73), which cleaves the ester linkages between ferulic acid and arabinosyl units on heteroxylans, may also increase enzymatic accessibility of the xylanase toward the heteroxylan fraction, thus releasing more XOS,[80,81] although this has not been shown in all cases.[82] While more XOS may be released with the addition of these enzymes, their structures and consequently their prebiotic and/or antioxidant properties may change substantially.

Autohydrolytic treatment has the advantage over enzymatic treatment in that it does not require the use of harsh chemicals or enzymes that can contribute substantially to cost.[72] Unfortunately, autohydrolysate liquors contain a variety of contaminants that must be removed. These contaminants are commonly removed by activated charcoal, ultrafiltration, ion exchange, etc.[83]

Two studies have reported the use of autohydrolysis to solubilize a portion of the heteroxylan fraction from corn bran or corn fiber.[84,85] When corn fiber was used as a starting material, a maximum solubilization of 300 g kg^{-1} of xylan occurred at 210 °C, but a substantial amount of monosaccharides was produced.[84] At 180 °C, xylan yield was lower (200 g kg^{-1}), but it contained a more desirable range of molecular weights. Using corn bran as a starting material, maximum solubilization of xylan occurred at 180 °C for 10 min or 200 °C for 2 min.[85] Under these conditions, about 500 g kg^{-1} of arabinoxylan was released into solution in the form of oligo- and polysaccharides. These liquors were accompanied by a monosaccharide contamination of about 100 g kg^{-1} of total neutral sugar residues in the starting material. These studies suggest that corn bran may be a better candidate for the production of XOS by autohydrolysis owing to higher yields.

Short-chain XOS from other agricultural products are potential prebiotics.[86] Prebiotics are indigestible oligosaccharides that selectively stimulate the growth of beneficial bacteria (e.g. bifidobacteria and lactobacilli) in the gastrointestinal tract of healthy persons.[87] In preliminary animal studies, XOS have been shown to stimulate the growth of bifidobacteria more than fructo-oligosaccharides, the most common and studied prebiotics.[88] In a study with aged men using a commercial XOS (Xylooligo 95P, Suntory Ltd, Osaka, Japan), concentrations of bifidobacteria were increased after 3 weeks on XOS.[89] XOS from corn bran or corn fiber exhibit similar structures to these prebiotic XOS, and this may also confer prebiotic properties.

In addition to prebiotic activity, XOS may contain antioxidant activity. Depending on production parameters, XOS produced from cereal brans may retain esterified ferulic acid moieties on the solubilized oligosaccharides. These XOS exhibit high antioxidant activity *in vitro*[90–92] and, despite the antimicrobial effects of ferulic acid,[93] do not appear to inhibit the growth of probiotic bacteria in pure culture.[94] In the large bowel of rats, microbial esterases are able to release the ferulic acid moiety, where it acts as a local antioxidant or may be absorbed and transported to other tissues.[95] This has potential implications for the prevention of inflammatory diseases and cancer.[66] Notably, corn bran contains more ferulic acid than many common cereal brans, fruits and vegetables.[96] Thus XOS with bound ferulic acid from corn bran have the potential to exhibit higher antioxidant activity than those isolated from other agricultural products.

Corn fiber oil

Most corn oil for human consumption comes from the germ;[97] however, in recent years, corn fiber oil has received attention owing to its ability to lower cholesterol in animal studies.[98–100]

This is most likely a result of high levels of ferulate phytosterol esters,[101] the most predominant being sitostanyl ferulate.[102] Corn fiber contains three to six times more of these components than corn bran (Table 1). Unfortunately, the amounts are still quite low compared with the levels of similar type compounds in other bran-derived oils such as rice bran oil.[102] Therefore, before this product can obtain commercial application, ways to increase the oil yield and phytosterol content of the oil must be examined.

Singh *et al*.[103] explored the effects of adding different sulfates or acids to the steep water during the wet-milling of two hybrids of corn. None of the sulfates increased oil yield, but ammonium sulfate increased ferulate phytosterol ester yield. Of the acids tested, acetic and hydrochloric acids appeared to be the most effective at increasing oil yield and phytosterol content of the oil.

Acids or enzymes added to the corn fiber itself may affect oil yield and composition. Singh *et al*.[104] treated corn fiber that had been conventionally wet-milled with sulfuric acid or a mixture of cellulase, amylase, xylanase and β-glucosidase. They found that each of these treatments increased the oil and phytosterol content of the corn fiber by up to sevenfold by hydrolyzing and removing a portion of the non-oil components (e.g. starch, cellulose, hemicellulose).

Non-chemical treatments to increase oil yield of corn fiber have been investigated. Wu and Norton[105] used fine grinding and air classification to fractionate corn fiber. They found that the finest particles ($<$30 µm) were highest in ferulate phytosterol esters. Moreau *et al*.[106] tested the effects of heat treatments in conventional, vacuum and microwave ovens. They found that none of the treatments substantially impacted oil yield but that the conventional and vacuum oven treatments slightly decreased phytosterols and substantially increased γ-tocopherol. They concluded that the decreases in phytosterols were practically insignificant and that the treatments were useful for increasing γ-tocopherol (an antioxidant) in corn fiber oil.

Ferulic acid

Ferulic acid is a phenolic antioxidant.[107] In comparison with other naturally occurring antioxidants, including gallic acid, caffeic acid, malvidin, delphinidin, catechin, epicatechin, rutin and quercetin, ferulic acid has been shown to be the most efficient in inhibiting lipid and protein oxidation in a lecithin/liposome oxidation system.[108] Ferulic acid also possesses antimicrobial activity against spoilage and pathogenic micro-organisms.[109,110] Because of its antioxidant and antimicrobial properties, ferulic acid has great potential for use in the food industry as a preservative.[111]

Ferulic acid may also be used in the production of vanillin, in edible films, as a crosslinking agent and as a supplement.[111] The use of ferulic acid as a precursor for natural vanillin production will be discussed in a later section. In edible films, ferulic acid has been shown to increase tensile strength and per cent elongation at break and decrease water vapor permeability and gas permeability in edible films created from soy protein isolate.[112] Ferulic acid addition to milk has been shown to enhance heat stability, possibly by crosslinking nucleophilic amino acid residues on κ-casein, thus preventing dissociation.[113] As a supplement or drug, ferulic acid may theoretically be useful in the treatment of Alzheimer's disease, diabetes, some cancers, hypertension, atherosclerosis and inflammatory diseases.[96]

Commercially, ferulic acid can be synthesized by a condensation reaction of vanillin with malonic acid catalyzed by piperidine.[114] However, the cost of this procedure, environmental concerns and the desire for naturally derived food additives make isolation of ferulic acid from natural sources desirable. Indeed, ferulic acid has been produced commercially in Japan by saponification of the product of rice bran oil refining[107]. Interestingly, rice bran oil contains 10–20 g kg^{-1} ferulic acid,[107,111] whereas corn bran contains more than 30 g kg^{-1} ferulic acid (Table 1) and is the best source of ferulic acid among common cereals, fruits, vegetables and other agricultural products.[96] Unfortunately, ferulic acid in corn bran is largely bound to cell wall components,[27,28] thus creating technological challenges for its isolation from corn bran.

Much of the research surrounding ferulic acid utilization from corn bran has focused on its release from its bound state. In a process similar to the production of corn fiber gum (discussed above), corn bran may be treated with alkali to cleave the ferulate crosslinks,[13] thus releasing ferulic acid into solution. In this case, ferulic acid and corn fiber gum are co-solubilized and can be separated by precipitating the corn fiber gum with ethanol.[13] Saulnier *et al*.[13] found a maximum release of ferulic acid from corn bran with 0.5 mol L^{-1} sodium hydroxide at 30 °C for 2 h, while only 30% of the corn bran gum fraction was co-solubilized. Thus, if corn bran gum is also desired, a harsher alkali treatment is required to release the heteroxylan fraction in higher yields.[14] Tilay *et al*.[115] used response surface methodology to maximize the release of ferulic acid from corn bran. They found that 4 mol L^{-1} sodium hydroxide at 21.6 °C for 24 h led to a 1.3-fold increase in the level of ferulic acid recovered compared with the unoptimized procedure, which was 2 mol L^{-1} sodium hydroxide at room temperature for 24 h. The authors reported ferulic acid at 191.1 g kg^{-1} corn bran under the optimized conditions. These levels are much lower than typically reported for corn bran, but comparable to corn fiber (Table 1). Therefore these authors may unknowingly have used corn fiber instead of corn bran, or the corn bran may have been old and undergone significant storage-related oxidation. The fact that the optimized extraction conditions are so different from those reported previously by Saulnier *et al*.[13] suggests the former explanation.

Ferulic acid can also be liberated from corn bran by microbial enzymes, namely feruloyl esterases.[116–118] Feruloyl esterases catalyze the cleavage of the ester linkage between ferulic acid and the arabinosyl moiety on arabinoxylans. These extracellular enzymes are produced from a number of bacteria and fungi when grown on substrates containing bound ferulic acid.[116,118,119] Feruloyl esterases have been classified into types A, B, C and D based on their specificity for aromatic substrates and sequence similarities with other enzyme classes.[116] Types A and D are able to cleave ferulic acid dimers such as those that form the crosslinks in corn pericarp cell walls, while all classes are able to release ferulic acid. Type A shares sequence similarity with lipases, while type B is similar to carboxylic esterase family 1. Types C and D show sequence similarities with chlorogenate esterase and xylanase respectively.

Microbial feruloyl esterases alone are not sufficient to release significant amounts of ferulic acid from corn bran;[120] other treatments and cell wall-degrading enzymes must be used in concert with feruloyl esterases if sufficient yields are to be realized. For example, Bonnin *et al*.[15] were only able to release 30 g kg^{-1} of insoluble, esterified ferulic acid from corn bran when incubated with an enzyme preparation from *A. niger* I-1472. However, when the corn bran was treated by autoclaving at 160 °C for 1 h, the enzymes were able to release 903 g kg^{-1} of esterified ferulic acid from the fraction of corn bran that had been solubilized by autoclave treatment. Using Novozym 342, Saulnier *et al*.[121] solubilized only 300 g kg^{-1} of insoluble ferulic acid from corn

bran, and about one-third of the ferulic acid remained esterified to arabinose. Upon pre-treating the corn bran by autoclaving at 160 °C for 1 h or flash-explosion at 190 °C for 1 min, 800 g kg^{-1} of insoluble ferulic acid was solubilized (free + esterified) and Novozyme 342 was then able to release about two-thirds of that ferulic acid as free ferulic acid. When feruloyl esterases are used in combination with other enzymes, the increased release of ferulic acid is the result of the production of short-chain feruloylated XOS, which are soluble and more accessible to feruloyl esterases.[122]

The above studies used a mixture of cell wall-degrading enzymes in addition to pre-treatments of the corn bran in order to facilitate enzymatic attack.[15,121] This is because, in general, corn bran has proven a more difficult substrate for enzymatic degradation compared with others such as wheat bran.[23] Using a crude enzyme preparation from *Neosartorya spinosa* NRRL 185, however, Shin *et al*.[23] were able to release 988 g kg^{-1} of insoluble, esterified ferulic acid as free ferulic acid from corn bran without pre-treatment.

BIOCONVERSION OF CORN BRAN AND CORN FIBER COMPONENTS

Most of the research on bioconversion of corn bran and corn fiber has focused on the production of fuel ethanol;[11,12] however, components of these co-products may be converted to other chemicals that would be important to the food industry. The use of corn bran or corn fiber as a starting material for food additive/chemical production has numerous potential advantages such as reduced environmental impact, 'natural' label and increased revenue for producers of corn products.

Xylitol

Xylitol is a five-carbon polyalcohol that occurs widely in nature.[123] In the food industry, xylitol is used as a low-calorie, non-cariogenic sweetener with bulking properties similar to those of sucrose.[124] Xylitol is not used by plaque-causing bacteria in the mouth and thus does not promote dental caries; it is also useful for diabetic foods owing to its slow absorption and low impact on glycemic index.[124]

Commercially, the majority of xylitol is produced by chemical hydrogenation of xylose, usually obtained from wood hydrolysates. Corn bran and corn fiber offer promising starting materials for xylose harvest owing to their high xylose content (~200 g kg^{-1}, Table 1), which is comparable to that of hardwoods.[125]

Xylose from acid hydrolysates must be purified prior to chemical hydrogenation, because the presence of other materials impedes the conversion and crystallization of xylose.[124] This costly and technically challenging step, as well as environmental concerns related to chemical hydrogenation, has sparked interest in the microbial conversion of xylose to xylitol in a process similar to the production of ethanol. In this case the starting material is hydrolyzed using dilute acid or enzyme treatment and then the resulting syrup is fermented with a yeast such as *Candida tropicalis*.[126] As with the conversion of pentose sugars to ethanol, yields of xylitol are generally low because of the formation of inhibitors such as furfural and hydroxymethylfurfural during hydrolysis.[126] To overcome the effects of inhibitors, Buhner and Agblevor[127] treated corn fiber hydrolysates with activated charcoal to remove these inhibitors. They found that activated charcoal was effective at removing inhibitors and increasing xylitol yield. Improved processes and yeasts for the conversion of xylose to xylitol would be important.

Vanillin

Vanillin is the major flavor component in properly cured vanilla (*Vanilla planifolia* Andrews) pods and occurs at 10–30 g kg^{-1} whole bean.[128] Vanillin also occurs at lower concentrations in a wide variety of other agricultural products, including ponderosa pine (*Pinus ponderosa*), tobacco and citrus fruits;[129,130] even corn bran itself contains a small amount of vanillin (55 g kg^{-1}).[131]

In the food, pharmaceutical and cosmetic industries, vanillin is an important flavor and aroma compound.[132] In these industries the demand for vanillin far outweighs its production from vanilla beans; therefore synthetic (or artificial) vanillin is often used.[128] Between the 1930s and 1980s in the USA, most of the synthetic vanillin was produced from spent sulfite liquors; however, owing to environmental concerns, this process has been abolished.[129] Today, synthetic vanillin is produced from guaiacol using petroleum as the carbon source.[128,129] Owing to the desire for natural vanillin production with less environmental impact, researchers have turned to ferulic acid as a possible starting material, which can be converted to vanillin by microbiological means.[133–135] Hence, owing to its high ferulic acid content, corn bran may play a critical role in supplying ferulic acid for the biosynthesis of vanillin.

As mentioned, the ferulic acid in corn bran is covalently linked to arabinosyl moieties as a glycosidic conjugate[27,28] and thus must be liberated from its bound state. Alkaline hydrolysis can accomplish this task;[13,115] however, ferulic acid obtained in this manner cannot be considered natural.[136] For a natural claim, ferulic acid and other potential food additives must be obtained by physical, enzymatic or microbiological means.[137]

Lesage-Meessen *et al*.[137] used a three-step process to convert ferulic acid from corn bran to vanillin. The first step involved autoclaving corn bran at 140 °C for 3 h and recovering the solubilized feruloylated oligosaccharides, which represented 300 g kg^{-1} of total ferulic acid originally present in the corn bran. Enzymes harvested from *A. niger*, which had been grown on sugar beet pulp, were then added to a culture of *Pycnoporus cinnabarinus* containing the soluble feruloylated oligosaccahrides obtained from autoclaved corn bran. The *A. niger* enzymes released the ferulic acid from its carbohydrate moiety and converted the free ferulic acid to vanillic acid; *P. cinnabarinus* then converted the vanillic acid to vanillin with a molar yield of 22%. When *A. niger* itself, rather than its enzymes, was used to release ferulic acid and convert it to vanillic acid, followed by conversion with *P. cinnabarinus*, the molar yield increased to 43% when cellobiose and XAD-2 resin were also added to the culture medium.

As discussed previously, enzyme extracts from *N. spinosa* NRRL 185 were able to release 988 g kg^{-1} of total ferulic acid as free ferulic acid from corn bran without pre-treatment.[23] The ferulic acid thus obtained was then added to a culture of *Streptomyces setonii* ATCC 391 161. After 12 h, 43% of the ferulic acid had been converted to vanillin; however, substantial levels of vanillic acid and other contaminants were also produced.

Buranov and Mazza[131] recently reported a possible non-microbiological method of converting ferulic acid to vanillin that would still be considered natural. This involves the direct conversion of bound ferulic acid to vanillin using pressurized low-polarity water extraction (also known as subcritical water extraction). In this process, water at high temperature was kept under sufficient pressure to maintain it in its liquid state while passing through a column containing the sample. Buranov and Mazza[131] hypothesized that, under these conditions, some of the ferulic acid was liberated from its bound state by cleavage

of its aliphatic double bond rather than the ester linkage, thus producing vanillin. The highest vanillin production (1.68 g kg^{-1} corn bran) was obtained using water at 220 °C, 5.2 MPa and a flow rate of 5 mL min^{-1} for 40 min. This represents a poor yield, as the corn bran starting material contained 25.1 g ferulic acid kg^{-1}. The authors suggest that yields may be improved by optimizing processing conditions and/or adding 'green' additives.

CONCLUSIONS

Wet-milling and dry-milling of corn result in a variety of co-products that are currently sold as animal feeds and other low-value commodities.[6,7] Utilization of these co-products for food applications may increase the value of these mill streams, reduce agricultural waste and decrease the cost of major corn products. Two of these major co-products are corn bran and corn fiber.

Previous research has been devoted to direct addition of these mill streams to food,[30–34] fractionation of each co-product to recover potentially useful components[8,10,14,17,24,52,58–60,84,85,101,103,104,106] or conversion of these components to other commercially important chemicals.[23,127,131,137] Corn fiber oil, with its high levels of ferulate phytosterol esters, may help lower cholesterol,[98–100] while phenolic acids, richly contained in corn bran, may be used as preservatives, as crosslinking agents, as supplements or as precursors to natural vanillin production.[111] The dietary fiber fraction of each co-product can be fractionated to yield corn fiber gum with low viscosity and excellent emulsifying properties[59,60] or cellulosic fiber gels with properties similar to shortening in baked goods.[52,55] The heteroxylan fraction can be partially hydrolyzed to yield potential prebiotics[86] or completely hydrolyzed and converted to food ingredients.[127]

With the exception of cellulosic fiber gel (Z-Trim) produced from corn bran,[52] the commercial implementation of these applications has not been realized owing to the numerous challenges involved in working with these co-products. Important areas of future research may include the following: (1) improved techniques beyond extrusion for increasing functionality of these whole co-products in foods; (2) ways to increase corn fiber oil yield and maximize the phytosterol content; (3) improved methods for the solubilization or partial hydrolysis of the heteroxlyans in corn bran or corn fiber to yield corn fiber gum or XOS; (4) more cost-effective ways of liberating and purifying ferulic acid and other phenolic acids; (5) improved methods for the complete hydrolysis of heteroxylans for conversion to xylitol or other food chemicals; (6) identification of more productive strains of microorganisms that are capable of converting components of corn bran to potentially useful food products.

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